Batch Adsorption Kinetics of Zinc Ions Using Activated Carbon from Waste Nigerian Bamboo

Ademiluyi F.T, Alex Abidde

Abstract— Batch adsorption kinetics of Zinc ions using activated carbon from waste Nigerian bamboo was investigated. The bamboo was cut into sizes, washed, dried and carbonized at 300oC-500oC. It was then activated at 800oC using nitric acid. The effect of contact time on the adsorption of zinc ions in aqueous solution was also investigated and were found to significantly affect the adsorption capacity of zinc ions . The adsorption process fitted well into the Freundlich, and Langmuir isotherm models indicating a monolayer formation over the surface of the material. Langmuir isotherm had monolayer saturation capacity of 250 mg/g of zinc ions adsorbed per g of bamboo activated carbon and high adsorption intensity of 1.579. In order to determine the mechanism of sorption, kinetic data were modeled using the pseudo first order , pseudo second order kinetic equations, and intra-particle diffusion model. The pseudo second order equation was the best applicable model to describe the sorption process. Hence the pseudo second order kinetic reaction is the rate controlling step with some intra particle diffusion taking place during the adsorption.

Index Terms— Nigerian Bamboo, Activated Carbon, Kinetics, Zinc ions, Adsorption Isotherm.

I. INTRODUCTION

Zinc is one of the heavy metals considered toxic to plants, invertebrates, and even vertebrate fish. Though zinc is useful to man but excess amount of zinc ions in waste waters may cause zinc toxicity which could lead to severe hemolytic anemia, liver and kidney damages; vomiting and diarrhea [1]. Zinc oxide is widely used as a white pigment in paints, and as a catalyst in the manufacture of rubber [2]. High release of zinc ions into the environment is also toxic to agricultural activities, sediment entrainment and groundwater. As a result of this inevitable development due to industrial discharge, a few techniques for the removal of these heavy metals (lead, zinc, zinc, Nickel, chromium, mercury, cadmium, aluminum, manganese and cobalt) were introduced by concerned researchers for the removal of these heavy metals from untreated water. These methods are reverse osmosis, ultra filtration, nano-filtration, coagulation, sedimentation, adsorption, etc. Though, it was discovered that these methods have been proved to have a lot of disadvantages which includes cost of operation and production of post sludge. Among the aforementioned treatment methods, adsorption had been reported as an efficient and economic option [3,4] especially when the source of adsorbent is economical.

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Adsorption is one of the cheap and most effective methods in water purification and activated carbon is preferred adsorbent that is wildly used to treat waste water containing different classes or types of metal ions. Activated carbon has the tendency of adsorbing large and small dissolved organic molecules such as gases, chemicals and metal ions.

Different adsorbent has been reported for the removal of zinc ions in solution. High removal of zinc from water was achieved using acid treated Carbon Nanofibers [1]. Results of the study showed that, 97 % of zinc was removed by using COOH-CNFs a Carbon Nanofibers at pH 7, 150 rpm, and 2 hours. Process optimization of the removal of Zn (II) by activated carbon prepared from rice husk using chemical activation was also reported. [5]. The adsorption of Zinc, Cadmium and Nickel from aqueous solution using ground water sludge (GWS) as the adsorbent [6]. In this study, the adsorbent concentration (GWS) were varied from 250 mg/L to 400mg/L and agitated with aqueous solutions of heavy metal for 1 hr, 3hrs, 6 hrs, and 24 hrs contact time. It was found that adsorption of metal ions also increased with longer contact time and higher adsorbent dosages. The removal efficiencies for Cd, Ni and Zn at adsorbent concentration of 3000 mg/L, 3,500 mg/L and 4,000 mg/L, were found to be 91.6%, 73.8% and 69% respectively.

Batch sorption of Cu2+ and Zn2+ ions in aqueous solutions was investigated under different pH value, adsorption time, original content of metal ions, sorbent amount, and temperature using activated carbon, prepared from Typha latifolia [7] . Nigerian bamboo has been reported to be effective in the removal of heavy metals [8]. but the kinetics of the zinc ions from aqueous solution using activated carbon from Nigerian bamboo has not been studied.
Therefore the objectives of these work is to study the kinetics of the removal of zinc ions using activated carbon from Nigerian bamboo.

II. MATERIALS AND METHODS

A. Materials

The following materials and apparatus were used for this work: waste Nigerian based bamboo from a construction site on campus. Nitric acid was used as activating agents, A pyrolytic reactor was used for carbonization with condenser. Other materials used are heating mantle, desiccators, crucibles, funnels, and filter papers. Two electronic weighing balance, Ohaus top loading balance (+0.01) was used to weigh the bamboo before pyrolysis, while a more sensitive electronic analytical weighing balance (+0.001, Adams AFP 360L) was used for other analysis, retort stand, thermocouple with temperature sensor, spatula, crusher, sieves, measuring cylinders, and petri dish.

B. Carbonization

2kg of waste bamboo was cut into small sizes, washed, and dried. They were carbonized differently in a pyrolytic reactor at about 300–500°C for about two hours after which the charred products were allowed to cool to room temperature. The charred material was crushed and sieved.

C. Chemical Activation

The carbonised waste bamboo were weighed separately and poured in different beakers containing known quantity of trioxonitrate (v) acid. The best concentrations of the acid used for activation were already determined before this study [9]. The content of the beakers was thoroughly mixed until a paste was formed. The paste of the sample were then
transferred to crucibles and were placed in a Muffle furnace and heated at 800°C for two hours. The activated sample were then cooled at room temperature, washed with distilled water to a pH of 6-7, and dried in an oven at 105°C for three hours. The final products were sieved to same particle size, kept in an air tight polyethylene bags, ready for use

Fig 1 Pieces of Nigerian waste bamboo before, after carbonization and after activation.

D. Adsorption of Zinc ions in Aqueous Solution on Activated Carbons

Stock solution of zinc solution was prepared by dissolving 1g of salt containing zinc II ions into 1 litre of distilled water. 1g of activated carbon was measured and poured into 100ml of the zinc salt solution inside the flask. The adsorption was carried out initially for 15mins and filtered at room temperature of 30oC. The above procedure was done for 30 minutes, 45 minutes, 60 minutes, 90 minutes, 120 minute and 180 minutes till equilibrium was reached and was repeated for different concentration of zinc ions in solution. The adsorption of zinc in aqueous solution on bamboo activated carbon was carried out by studying the effect of various physicochemical parameters such as particle size, carbon dosage, initial concentration , contact time on the adsorption process.

The amount of zinc ions in solution (i.e., Zn2+) was determined using conductometric method from the filtrate after adsorption using waste Nigerian based bamboo. As described in the work of Banjonglaiad et al., [10] at low concentrations, conductivity is linearly related to the different metal ion concentrations so that if just one metal is present its concentration is readily established through calibration. Hence a calibration curve of zinc ion concentration versus conductivity was first prepared for each metal ion, before the kinetic study.

The amount of zinc ions adsorbed at equilibrium, Q eq (mg/g) was determined using equation

$$Q_e = \frac{(C_o - C_e)V}{m} = \frac{metal \text{ ion uptake (mg)}}{\text{g of carbon}} \quad (1)$$

and the percent zinc ion adsorbed (%) was computed as follows [11] :

$$\text{Percent adsorption (\%)} = \frac{(C_o - C)}{C_o} \times 100 \quad (2)$$

where Co and Ce are the initial and equilibrium concentrations (mg/L), V volume of solution, m the weight of activated carbon (g) and C the solution concentration at the end of adsorption

E Adsorption Isotherms modeling

The most commonly used isotherms in adsorption studies was used to fit the experimental adsorption data namely : Langmuir, and Freundlich Isotherms

The Langmuir isotherm was expressed as [12]:

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a_L Ce}{K_L} \quad (3)$$

where Qe is the amount of zinc ion adsorbed per unit mass of adsorbent (mg/g) at equilibrium, Ce is the equilibrium concentration of the adsorbate (mg/L)

KL = A constant related to the affinity between the adsorbent and the adsorbate (L/mg)

Qmax= KL/ aL = The theoretical monolayer saturation capacity.

The values of Qmax and KL can be determined by plotting Ce / Qe versus Ce

One of the most important parameter in the Langmuir isotherm model is the seperation factor RL which is a dimensionless factor defined as [13]

$$R_L = \frac{1}{1 + a_L C_o} \quad (4)$$

where: Co is the initial adsorbate concentration of zinc ions and aL is the Langmuir constant related to the energy of adsorption. The values of RL indicate the nature of the isotherm to be either unfavorable (RL> 1) , favorable (0 < RL < 1), linear (RL = 1), or irreversible (RL = 0).

The linear form of the Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as

$$Log \, Q_e = Log \, K_f + \frac{1}{n} Log \, C_e \quad (5)$$

Kf = The Freundlich constant related to the adsorption capacity

1/n= The Freundlich constant related to the adsorption intensity.

F Kinetic study

Three kinetic models were used in this study to model the adsorption of zinc II ion on bamboo activated carbon namely:

pseudo first order, pseudo second order and the intra particle diffusion models.

a) The pseudo first order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites.

$$\ln (Q_e - Q_t) = \ln Q_e - K t \qquad (6)$$

b) The Pseudo Second order kinetic model for adsorption of zinc is expressed as [14]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (7)$$

Intra -particle diffusion may be the rate determining step in batch adsorption process the uptake of adsorbate varies with the square root of the adsorption time [14] .

where, Qe is the mass of metal adsorbed at equilibrium (mg/g), Qt (mg/g) is the mass of metal adsorbed at time t and K is the first order reaction rate constant (L/min). A straight line of ln (Qe - Qt) verses t indicates the application of the first order kinetic model .

so that
$$Q_t = k_2 t^{0.5} + C \qquad (8)$$
A linear plot of Qt versus t0.5 shows that the adsorption mechanism follows intra -particle diffusion and if the intra -particle diffusion is the rate controlling step , the line would passes through the origin.

III. RESULTS AND DISCUSSION

A. Effect of Contact Time on Batch Adsorption of Zinc ions in Aqueous Solution

Figure 2 shows the effect of contact time on the adsorption of zinc ions solution using activated carbon from Nigerian bamboo. The concentrations of zinc ions in solution was varied from 28mg/L to 227mg/L and batch adsorption was carried out with 1g of activated bamboo. The percentage of zinc ions adsorbed increased with time until equilibrium was reached for each concentrations. It is therefore evident from Fig 2 that at low concentration ranges the percent adsorption is high because of the availability of more active sites.

At higher concentration of metal ion more and more surface sites are covered, the capacity of the adsorbent get exhausted due to non-availability of active surface sites. This leads to a fall in the percentage of metal ion adsorbed at higher concentration. It was observed that the percentage adsorption of zinc ion rapidly reached equilibrium at 30 minutes of contact for 28mg/L concentration, it increased to 100% implied that zinc ion was completely removed from aqueous solution at this concentration
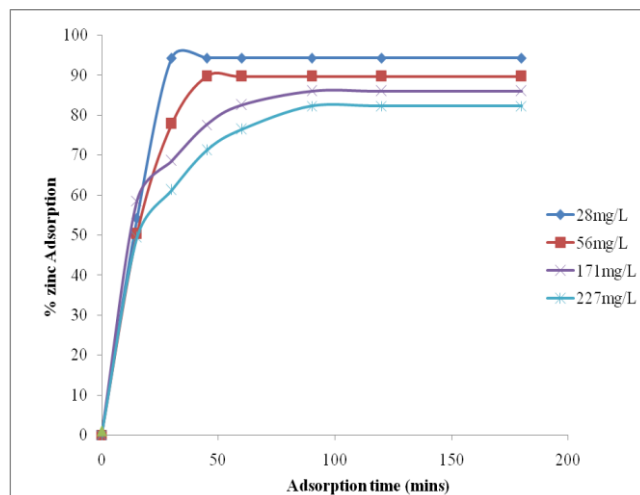

Figure 2 Effect of Contact Time on the Adsorption of Zinc (II) ions using waste Nigerian Bamboo Carbon

This is because at this time equilibrium is established. The delay in equilibrium condition at higher concentrations may be attributed to the few available sites of adsorptions. Beyond this optimum contact time it is evident that the surface of the adsorbent becomes more and more saturated due to the availability of many active sites.

B. Adsorption Isotherms

C. Langmuir Adsorption Isotherm for Zinc ion

Fig 6 shows the Langmuir adsorption isotherm for the adsorption of Zinc ions on bamboo activated carbon. the equilibrium concentration of zinc ions in solution (Ce) varies linearly with the ratio of the equilibrium concentration and the amount of zinc ions adsorbed (Ce/Qe). The linearity of the plot shows that Langmuir isotherm model can be used to predict the sorption of zinc ions on bamboo activated carbon. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interactions between adsorbed ions [15]. The Langmuir model parameters and the statistical aspect of the adsorption data is presented in Table 2 and the correlation coefficient R2 of 0.995 which reveals that the isotherm is consistent with Langmuir model. The adsorption capacity Qmax for zinc represents a practical limiting adsorption capacity when the surface is fully covered with heavy metal ions and assists in the comparison of adsorption performance [11].

The adsorption capacity Qmax of activated carbon from bamboo was 250 mg/g of carbon. It was obtained from the reciprocal of the slope of Fig 3. This value is higher than the value obtained by Kalavathy et al., [16], in which Qmax value of 22.03mg/g was obtained during the removal of Zn from aqueous solution using activated carbon from Hevea brasiliensis. It was also higher than the value obtained by Surya and Ramachandra [11] with a Qmax of 38.2mg/g at 30oC during the adsorption of zinc ions on Shorea Robusta Leaf Litter using phosphoric acid impregnation. The maximum adsorption capacity observed during the adsorption of Zn2+ ions onto biogenic elemental selenium nanoparticles (BioSeNPs) was 60 mg of Zinc adsorbed per g [18] .
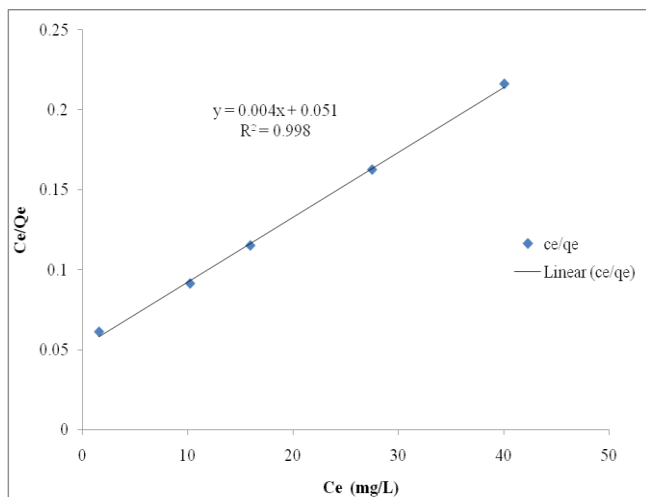
Fig 3 Langmuir adsorption isotherm for the adsorption of Zinc ions on bamboo activated carbon

The separation factor (RL) was determined from equation 4, the values were between 0.053 to 0.309 for adsorbate concentrations between 28 mg/L to 227mg/L. Since RL is less than 1 for all the concentrations it means that adsorption process is favorable.

D. Freundlich Adsorption Isotherm for Zinc ion

The batch adsorption isotherm of zinc ions on bamboo activated carbon at 30 oC is presented in Fig 4 . The log of Qe amount of zinc adsorbed at equilibrium was plotted against the log of the equilibrium concentration Ce of the metal ion adsorbed. The adsorption capacity Kf and the adsorption intensity 1/n were obtained directly from the slopes and intercepts of the linear plot. The linearity of the plot and high correlation coefficient R^2 obtained (0.995) reveals that the isotherm is consistent with Freundlich model . The value of adsorption intensity i.e n = 1.579 from Table 2   is more than one for bamboo activated carbon , indicating the adsorption zinc ion using bamboo activated carbon is   more of chemisorptions than physical adsorption .
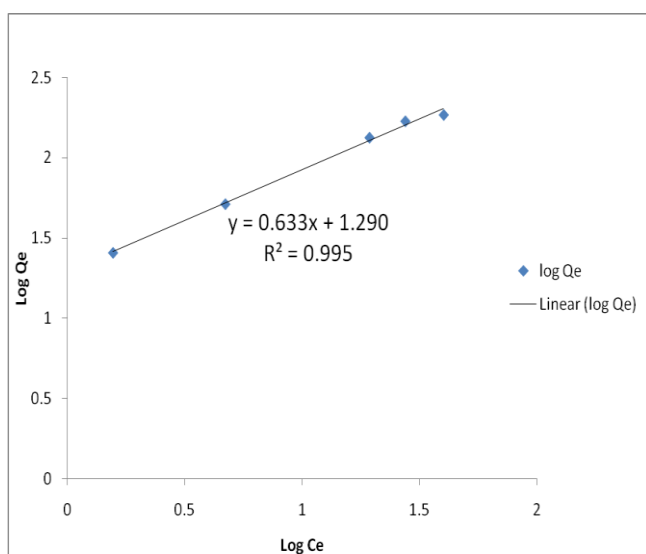

Fig 4 Freundlich Isotherm adsorption of zinc from aqueous solution using activated carbons from bamboo

Table 2 Constants and values from Isotherms Models for adsorption of zinc from aqueous solution using activated carbons from waste Nigerian bamboo

S/No	Isotherm Constants	Values
1.	langmuir $Q_{max}= K_L/a_L$ (mg/g) KL (L/mg) R2	250 19.608 0.998
2.	Freundlich n Kf R2	1.579 19.498 0.995

E. Adsorption Kinetic Models

The kinetic plots for the adsorption of zinc II ions on activated carbon from Bamboo using the pseudo first order, pseudo second order and the intra particle diffusion models at different concentrations is presented in Figures 5, 6 and 7. All concentration of zinc ions in solution below 100mg/L were not captured in Fig 5 and Fig 7 for the kinetic plot for first order and Intra particle diffusion kinetic models because the values were too small. The Pseudo first order kinetic and Intra particle diffusion kinetic models can only be used for zinc at high concentrations, unlike the Pseudo second order kinetic model for the batch adsorption of zinc ions shown in Fig 6 which accommodates wide range of zinc ion concentrations in aqueous solution as shown in Fig 6.
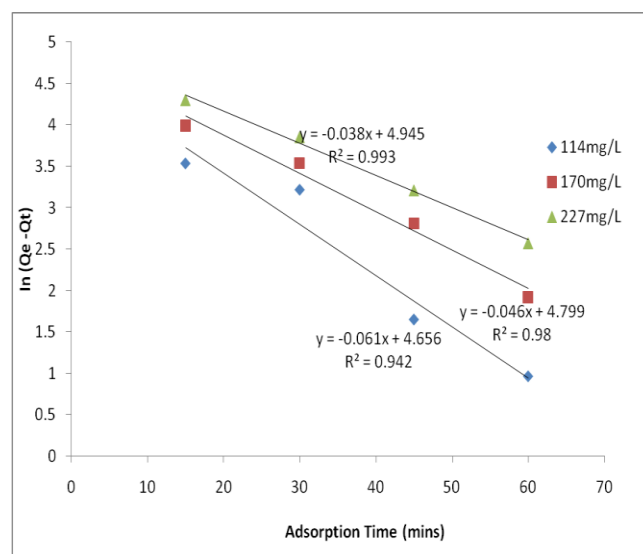

Fig 5 Pseudo first order kinetic plot for the batch adsorption of zinc ions at different concentrations of adsorbate at 30oC

Figures 6   also shows that the concentration of adsorbate affected the adsorption and diffusion process greatly since the slope and intercept are not the same at the different concentrations. The pseudo second order kinetic model gave a higher correlation coefficient R^2 at all concentration than the pseudo first order and the intra particle diffusion models as shown in Fig 6.

The linearity of plot of Qt versus $t^{0.5}$ in Fig 7 shows that the adsorption mechanism follows intra -particle diffusion but the line of the plot in Fig 11 did not pass through the origin. The values obtained from the intercept (64.09, 76.19, and 80.46) of the intra particle diffusion kinetic model at different adsorbate concentrations are not the same as shown in Fig 7 and did not pass through the origin which indicated intra -particle diffusion is not the rate controlling step.
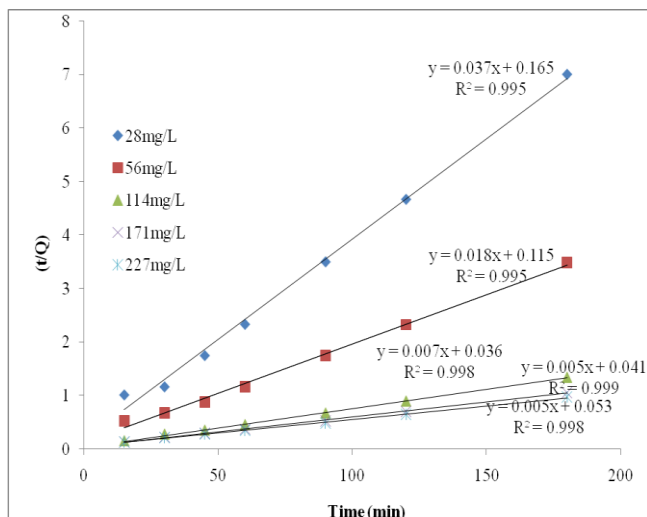
Fig 6 Pseudo second order kinetic plot for the batch adsorption of zinc ions at different concentrations of adsorbate at 30 oC
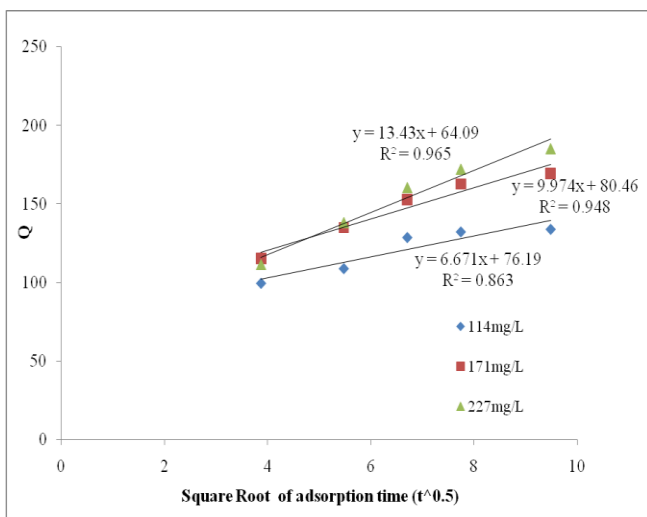

Fig 7 Intra particle diffusion kinetic model plot for the batch adsorption of zinc ions at different concentrations of adsorbate at 30oC

Thus pseudo second order kinetic is the rate controlling step. Also the values of the intercept of Fig 7 at the different concentrations gives an idea of the thickness of the boundary layer, the larger the intercept the thicker the boundary layer effect [17] . The values obtained from the intercept from Fig 7 (64.09-80.46) are significant, which revealed that the boundary is thick. Hence the pseudo second order kinetic reaction is the rate controlling step with some intra particle diffusion taking place.

IV. CONCLUSION

Zinc II ions batch adsorption kinetics from aqueous solution using activated carbon from waste Nigerian based bamboo has been investigated. The amount of zinc II ions adsorbed was found to vary significantly with contact time. The adsorption process fitted well into Langmuir, and Freundlich isotherms models. The monolayer saturation capacity of 250 mg of zinc II ions adsorbed per g of bamboo activated carbon was obtained and found to be higher than monolayer saturation capacity of other adsorbent used for zinc II ions adsorption. Adsorption kinetics was modelled using the pseudo first order , pseudo second order kinetic equations, and intra-particle diffusion models. sorption kinetics showed good agreement with experimental data. The pseudo second order kinetic reaction is the rate controlling step with some intra particle diffusion taking place. The high adsorption intensity of bamboo activated carbon and its affinity for zinc II ions can help solve many adsorption challenges in the industry and in water purification processes.

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